Extraction of Alkali Metal Picrates with Benzo-18-crown-6 into Various Organic Solvents. Fundamental Equilibria which Govern the Highest Extraction Selectivity for K^+ among Alkali Metal Ions

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For the determination of the actual overall extraction equilibrium constant (K_{ex}) and the ion-pair formation constant (K_{MLA}) in water of a crown ether–metal salt 1 : 1 : 1 complex, a more completed method is established by considering the concentration of the resulting 1 : 1 : 1 crown ether complex and ion-pair formation between the uncomplexed metal ion and the anion in the aqueous phase. The theoretical predictions were verified experimentally by solvent extraction with benzo-18-crown-6 (B18C6), alkali metal (Na, K, Rb) picrates, and various diluents of low dielectric constant. The actual log K_{MLA} values in water at 25 °C of the 1 : 1 : 1 B18C6-alkali metal picrate complexes are 1.54±0.16 for Na, 3.30±0.20 for K, and 3.11±0.24 for Rb. The distribution constants of the 1 : 1 : 1 B18C6 complexes were calculated from the partition constants of B18C6, the formation constants in water of the B18C6-alkali metal-ion complexes, and the actual K_{ex} and K_{MLA} values obtained in this study. The distribution behavior of the 1 : 1 : 1 B18C6 complexes is explained based on regular solution theory. The molar volumes and solubility parameters of the complexes were determined. Moreover, the fundamental equilibria which govern the highest extraction selectivity of B18C6 for K^+ among the alkali metal ions were completely elucidated.

It is very difficult to determine ion-pair formation constants of crown ether–metal ion complexes with anions in water because of the low stability of the crown ether–metal ion complexes and the low solubility in water of many of crown ethers. In a previous paper,[1] a new equation was derived from regular solution theory[2] in order to determine the ion-pair formation constant (K_{MLA}) of a crown ether–metal salt 1 : 1 : 1 complex in water. Its predictions were verified experimentally by solvent extraction using benzo-18-crown-6 (B18C6), potassium picrate, and various organic solvents of low dielectric constant; the first approximate overall extraction equilibrium constants (K_{ex}) and ion-pair formation constant in water of the B18C6-potassium picrate 1 : 1 : 1 complex were determined.

In this study, for the determination of the actual K_{ex} and K_{MLA} in water of the 1 : 1 : 1 crown ether complex, a more complete method has been established by considering the concentration of the resulting 1 : 1 : 1 crown-ether complex and ion-pair formation between the uncomplexed metal ion and the anion in the aqueous phase. The theoretical predictions were verified experimentally by solvent extraction with B18C6, alkali metal (Na, K, Rb) picrates, and various diluents of low dielectric constant. It is impossible to measure the partition constant of the 1 : 1 : 1 crown-ether complex, due to its low stability in water. However, the distribution constants of the 1 : 1 : 1 B18C6-alkali metal picrate complexes can be calculated from the partition constants of B18C6, the formation constants in water of the B18C6-alkali metal-ion complexes, and the actual K_{ex} and K_{MLA} values obtained in this study. The partition behavior of the 1 : 1 : 1 B18C6 complexes can be explained by regular solution theory.[2] Moreover, the fundamental equilibria which govern the highest extraction selectivity of B18C6 for K^+ among the alkali metal ions were completely elucidated.

Experimental

Materials. Benzo-18-crown-6 was prepared according to a method of Pedersen.[3] The purity was checked by melting-point (43.1—43.7 °C) and elemental analyses. The product was dried at 40 °C in vacuo prior to use. All of the organic solvents were analytical-grade reagents. 1,2-Dichloroethane was purified by distillation, but the others were not purified. They were washed several times with deionized water prior to use. Picric acid and alkali metal hydroxides were of analytical grade.

Distribution Constants of B18C6. A 10 cm^3 portion of an organic solution of B18C6 and an equal volume of deionized water were placed in a stoppered glass tube (volume 30 cm^3), agitated in a thermostated water bath for 2 h at 25±0.2 °C, and centrifuged. The concentration range of B18C6 was from 1.5×10^{-4} M (1 M=1 mol dm^{-3}) to 1.5×10^{-3} M. For the *m*-xylene system, the B18C6 concen-

Table 1. Equilibrium Constants for 1 : 1 : 1 B18C6-Alkali Metal Picrate Complexes at 25 °C

No.	Solvent[a]	log K_{ex}[b]			log $K_{ex,ip}$		
		Na	K[c]	Rb	Na	K[c]	Rb
1	DCM	3.758 ±0.009	5.76 ±0.02	5.23 ±0.04	4.90	6.53	6.60
2	CF	3.27[d]	5.28[d]	4.93[d]	4.46[d]	6.11[d]	6.35[d]
3	1,1-DCE	—	5.54 ±0.01	—	—	5.24	—
4	1,2-DCE	3.886 ±0.007	5.73 ±0.03	5.32 ±0.03	4.51	5.99	6.18
5	CBu	3.121 ±0.009	5.185 ±0.009	4.548 ±0.005	2.11	3.81	3.77
6	BZ	3.162 ±0.003	5.054 ±0.006	4.49 ±0.01	2.72	4.25	4.29
7	TE	3.116 ±0.008	5.33 ±0.01	4.465 ±0.008	2.38	4.23	3.95
8	*m*X	3.139 ±0.008	5.23 ±0.02[e]	4.412 ±0.008	2.06	3.79[e]	3.56
9	CB	3.512 ±0.006	5.66 ±0.01	5.072 ±0.007	3.29	5.08	5.08
10	BB	3.515 ±0.008	5.646 ±0.009	5.091 ±0.008	3.27	5.03	5.07
11	*o*-DCB	3.633 ±0.007	5.767 ±0.005	5.24 ±0.02	3.48	5.25	5.32
12	DBE	2.47 ±0.02	4.59 ±0.04[e]	3.70 ±0.03	0.42	2.17[e]	1.87

a) DCM dichloromethane; CF chloroform; 1,1-DCE 1,1-dichloroethane; 1,2-DCE 1,2-dichloroethane; CBu chlorobutane; BZ benzene; TE toluene; *m*X *m*-xylene; CB chlorobenzene; BB bromobenzene; *o*-DCB *o*-dichlorobenzene; DBE dibutyl ether. b) Each value is the average of 10—20 measurements. The uncertainties are the standard deviations. c) Recalculated from the data on Ref. 1. d) Recalculated from the data on Ref. 4. e) This study.

tration in the aqueous phase was spectrophotometrically determined at 273 nm (ε=2.50×10^3 cm^{-1} M^{-1}). For the dibutyl ether system, the B18C6 in the organic phase was back-extracted into an aqueous phase, and the B18C6 concentration was measured. The distribution constants of B18C6 are listed in Table 3.

Extraction of Alkali Metal Picrates with B18C6. The experimental procedures were almost the same as those described in a previous paper.[1] Extractions were performed in the pH 10.5 to 12.0 region at 25±0.2 °C. Concentrations of B18C6, NaOH, KOH, RbOH, and picric acid were 1.0×10^{-5}—1.2×10^{-2} M, (1.0—8.3)×10^{-2} M, (5.8—6.8)×10^{-3} M, (5.8—6.0)×10^{-3} M, and (1.0—4.2)×10^{-3} M, respectively. In blank experiments, there was no extraction in the absence of B18C6.

Theory and Results

When equilibrium occurs between a very basic aqueous phase of monovalent metal picrate (MA) and an organic phase of B18C6 (L), the equilibrium constants are defined as

$$K_{\mathrm{ex}} = [\mathrm{MLA}]_{\mathrm{o}}/[\mathrm{M}^+][\mathrm{L}]_{\mathrm{o}}[\mathrm{A}^-], \tag{1}$$

$$K_{\mathrm{D,L}} = [\mathrm{L}]_{\mathrm{o}}/[\mathrm{L}], \tag{2}$$

$$K_{\mathrm{ML}} = [\mathrm{ML}^+]/[\mathrm{M}^+][\mathrm{L}], \tag{3}$$

$$K_{\mathrm{MLA}} = [\mathrm{MLA}]/[\mathrm{ML}^+][\mathrm{A}^-], \tag{4}$$

$$K_{\mathrm{D,MLA}} = [\mathrm{MLA}]_{\mathrm{o}}/[\mathrm{MLA}], \tag{5}$$

$$K_{\mathrm{MA}} = [\mathrm{MA}]/[\mathrm{M}^+][\mathrm{A}^-], \tag{6}$$

where the subscript "o" and the lack of a subscript denote the organic and aqueous phase, respectively. The dissociation of MLA into ML$^+$ and A$^-$ in the organic phases is neglected because of the low dielectric constants (ε_{r}) of the diluents used in this study. The overall extraction equilibrium constant (K_{ex}) can be written as

$$K_{\mathrm{ex}} = K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{ML}}K_{\mathrm{MLA}}K_{\mathrm{D,MLA}}, \tag{7}$$

where $K_{\mathrm{MLA}}K_{\mathrm{D,MLA}}=[\mathrm{MLA}]_{\mathrm{o}}/[\mathrm{ML}^+][\mathrm{A}^-]=K_{\mathrm{ex,ip}}$. The distribution ratio (D) of the metal is represented by

$$D = [\mathrm{MLA}]_{\mathrm{o}}/([\mathrm{M}^+]+[\mathrm{MA}]+[\mathrm{ML}^+]+[\mathrm{MLA}]). \tag{8}$$

In the case that $[\mathrm{M}^+]\gg[\mathrm{MA}]+[\mathrm{ML}^+]+[\mathrm{MLA}]$, Eq. 8 is transformed into

$$D = K_{\mathrm{ex}}[\mathrm{L}]_{\mathrm{o}}[\mathrm{A}^-]. \tag{9}$$

From the mass balances, $[\mathrm{M}^+]$, $[\mathrm{L}]_{\mathrm{o}}$, and $[\mathrm{A}^-]$ are given by

$$[\mathrm{M}^+]=([\mathrm{M}]_{\mathrm{t}}-[\mathrm{MLA}]_{\mathrm{o}})/\{1+a[\mathrm{L}]_{\mathrm{o}}+(K_{\mathrm{MA}}+b[\mathrm{L}]_{\mathrm{o}})[\mathrm{A}^-]\}, \tag{10}$$

$$[\mathrm{L}]_{\mathrm{o}} = ([\mathrm{L}]_{\mathrm{t}}-[\mathrm{MLA}]_{\mathrm{o}})/\{c+(a+b[\mathrm{A}^-])[\mathrm{M}^+]\}, \tag{11}$$

$$[\mathrm{A}^-] = ([\mathrm{HA}]_{\mathrm{t}}-[\mathrm{MLA}]_{\mathrm{o}})/\{1+(K_{\mathrm{MA}}+b[\mathrm{L}]_{\mathrm{o}})[\mathrm{M}^+]\}, \tag{12}$$

where $a=K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{ML}}$, $b=K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{ML}}K_{\mathrm{MLA}}$, $c=1+K_{\mathrm{D,L}}{}^{-1}$, and the subscript "t" designates the total concentration. As a first approximation, it is assumed that $1\gg a[\mathrm{L}]_{\mathrm{o}}+(K_{\mathrm{MA}}+b[\mathrm{L}]_{\mathrm{o}})[\mathrm{A}^-]$ (Eq. 10), $c+a[\mathrm{M}^+]\gg b[\mathrm{M}^+][\mathrm{A}^-]$ (Eq. 11), and $1+K_{\mathrm{MA}}[\mathrm{M}^+]\gg b[\mathrm{L}]_{\mathrm{o}}[\mathrm{M}^+]$ (Eq. 12). The $[\mathrm{L}]_{\mathrm{o}}$ and $[\mathrm{A}^-]$ values of Eq. 9 were calculated based on this assumption. Plots of $\log(D/[\mathrm{A}^-])$ vs. $\log[\mathrm{L}]_{\mathrm{o}}$ always give a straight line with a slope of 1 in every case, indicating the formation of a 1 : 1 complex of B18C6 with the metal ion and the validity of the above assumptions. The first approximate K_{ex} value for each system was determined based on these assumptions.

The distribution constant ($K_{\mathrm{D,L}}$) of B18C6 is estimated by the following equation derived from regular solution theory:[2]

$$RT\ln K_{\mathrm{D,L}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}}) = V_{\mathrm{L}}(\delta_{\mathrm{w}}-2\delta_{\mathrm{L}})+V_{\mathrm{L}}\delta_{\mathrm{o}}{}', \tag{13}$$

where $\delta_{\mathrm{o}}{}'=\delta_{\mathrm{o}}+RT(1/V_{\mathrm{o}}-1/V_{\mathrm{w}})/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$; δ_{w}, δ_{o}, and δ_{L} denote the solubility parameters of water, the organic solvent and B18C6, respectively; V_{L}, V_{o}, and V_{w} are the molar volume of B18C6, the organic solvent, and water, respectively. The distribution constant ($K_{\mathrm{D,MLA}}$) of a neutral ion-pair complex MLA is estimated by

$$RT \ln K_{\mathrm{D,MLA}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})=V_{\mathrm{MLA}}(\delta_{\mathrm{w}}-2\delta_{\mathrm{MLA}})+V_{\mathrm{MLA}}\delta_{\mathrm{o}}', \quad (14)$$

where V_{MLA} and δ_{MLA} designate the molar volume and solubility parameter of MLA, respectively. Combining Eqs. 13 and 14 leads to

$$\log K_{\mathrm{D,MLA}} = \{V_{\mathrm{MLA}}(\delta_{\mathrm{w}} + \delta_{\mathrm{o}}' - 2\delta_{\mathrm{MLA}}) / V_{\mathrm{L}}(\delta_{\mathrm{w}} + \delta_{\mathrm{o}}' - 2\delta_{\mathrm{L}})\} \log K_{\mathrm{D,L}}. \quad (15)$$

By adding $\log K_{\mathrm{MLA}}$ to both sides of Eq. 15, we obtain

$$\log K_{\mathrm{ex,ip}} = \{V_{\mathrm{MLA}}(\delta_{\mathrm{w}} + \delta_{\mathrm{o}}' - 2\delta_{\mathrm{MLA}}) / V_{\mathrm{L}}(\delta_{\mathrm{w}} + \delta_{\mathrm{o}}' - 2\delta_{\mathrm{L}})\} \log K_{\mathrm{D,L}} + \log K_{\mathrm{MLA}}. \quad (16)$$

In the case that the δ_{L} and δ_{MLA} values are nearly equal, Eq. 16 leads to

$$\log K_{\mathrm{ex,ip}} = (V_{\mathrm{MLA}}/V_{\mathrm{L}}) \log K_{\mathrm{D,L}} + \log K_{\mathrm{MLA}}. \quad (17)$$

Plots of the first approximate $\log K_{\mathrm{ex,ip}}$ values vs. $\log K_{\mathrm{D,L}}$ values in Figs. 1, 2, and 3 show a good linear relationship for the respective alkali metals, except for CF (the correlation coefficients r=0.985 for Na, 0.986 for K, and 0.985 for Rb). The first approximate $\log K_{\mathrm{MLA}}$ values are obtained from the intercepts of the $\log K_{\mathrm{ex,ip}}$ vs. $\log K_{\mathrm{D,L}}$ plots. The second approximate $[\mathrm{A}^-]$ value was calculated from Eq. 12 by using the first approximate values of $[\mathrm{M}^+]$, $[\mathrm{L}]_{\mathrm{o}}$, and K_{MLA}. The actual $[\mathrm{M}^+]$, $[\mathrm{L}]_{\mathrm{o}}$, $[\mathrm{A}^-]$, K_{MLA}, and K_{ex} values were calculated from Eqs. 1, 7, 10, 11, 12, and 17 by a successive-approximation method. The $\log K_{\mathrm{ex}}$ and $\log K_{\mathrm{MLA}}$ values are compiled in Tables 1 and 4, respectively. A better linear relationship is observed for the plots of the actual $\log K_{\mathrm{ex,ip}}$ values vs. $\log K_{\mathrm{D,L}}$ values for the respective alkali metals, except for CF (the correlation coefficients r=0.994 for Na, 0.987 for K, and 0.986 for Rb).

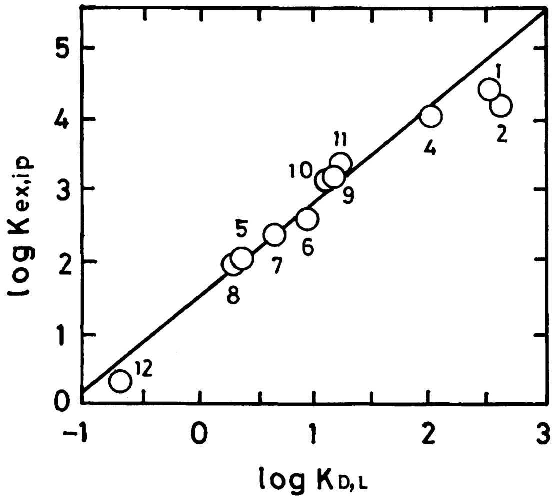

Fig. 1. Plots of first approximate $\log K_{\mathrm{ex,ip}}$ values vs. $\log K_{\mathrm{D,L}}$ values for B18C6-sodium picrate system. The numbers correspond to those in Table 1.

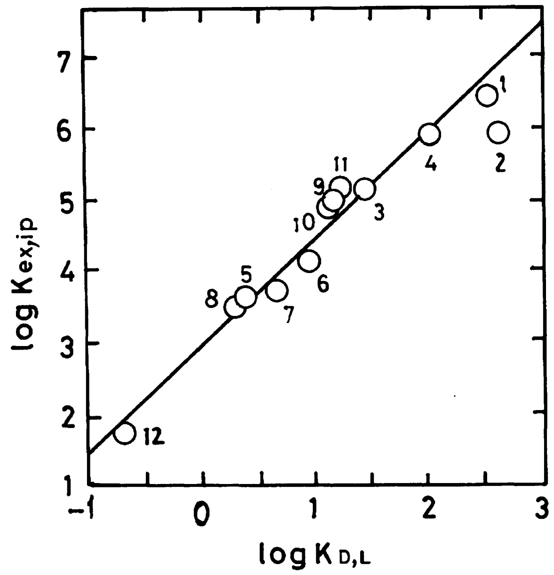

Fig. 2. Plots of first approximate $\log K_{\mathrm{ex,ip}}$ values vs. $\log K_{\mathrm{D,L}}$ values for B18C6-potassium picrate system. The numbers correspond to those in Table 1.

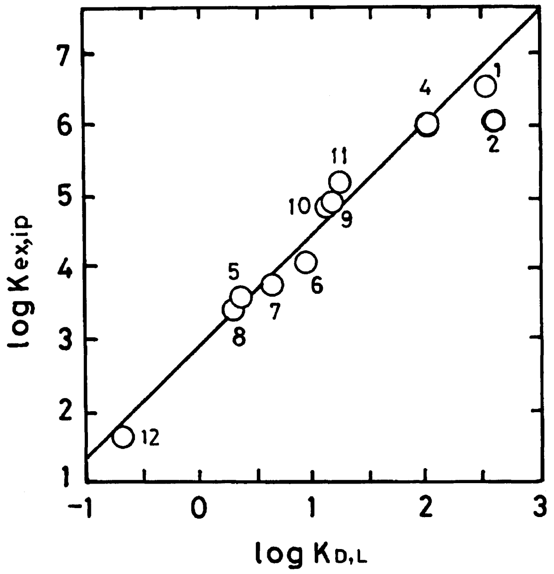

Fig. 3. Plots of first approximate $\log K_{\mathrm{ex,ip}}$ values vs. $\log K_{\mathrm{D,L}}$ values for B18C6-rubidium picrate system. The numbers correspond to those in Table 1.

Discussion

The $RT \ln K_{\mathrm{D,L}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ vs. δ_{o}' plots for B18C6 in Fig. 4 show a linear relationship, except for CF (the correlation coefficient r=0.948). The $K_{\mathrm{D,L}}$ values of mX and DBE determined in this study were added to the data of the previous work.[1] However, the V and δ values of B18C6 calculated from the slope and intercept (Table 4), respectively, are nearly identical with the V(249±36) and δ (11.5±0.5) values reported in the previous paper.[1]

The $\log K_{\mathrm{D,MLA}}$ values calculated from the $\log K_{\mathrm{ex,ip}}$ and $\log K_{\mathrm{MLA}}$ values are summarized in Table 3. From Figs. 5, 6, and 7, a linear relationship is found between $RT \ln K_{\mathrm{D,MLA}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ and δ_{o}' for the respec-

Table 2. Solvent Parameters at 25 °C

No.	Solvent	δ[a]	V[b]	E_T[c]	ε_r[d]
1	DCM	9.7	63.9	41.1	8.93
2	CF	9.3	80.7	39.1	4.81[e]
3	1,1-DCE	9.1	85	—	10.0[f]
4	1,2-DCE	9.8	79.4	41.9	10.36
5	CBu	8.4	104	—	7.39[e]
6	BZ	9.16	89.4	34.5	2.275
7	TE	8.93	106.9	33.9	2.379
8	*m*X	8.88	123.5	—	2.4
9	CB	9.5	102.1	37.5	5.62
10	BB	9.87	105	37.5	5.40
11	*o*-DCB	10.0	112.8	—	9.93
12	DBE	7.76	170.4	—	3.1
13	Water	17.55[g]	18.1	—	—

a) Solubility parameter ($\mathrm{cal^{1/2}\,cm^{-3/2}}$). Ref. 2. A. F. M. Barton, *Chem. Rev.*, **75**, 731 (1975). b) Molar volume ($\mathrm{cm^3\,mol^{-1}}$). R. C. Weast, "Handbook of Chemistry and Physics," 58th ed, CRC Press, Ohio (1977—1978) (density). c) Transition energy ($\mathrm{kcal\,mol^{-1}}$). C. Reichard and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968). d) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York (1970). e) 20 °C. f) 18 °C. g) T. Omori, T. Wakahayashi, S. Oki, and N. Suzuki, *J. Inorg. Nucl. Chem.*, **26**, 2265 (1964).

Table 3. Distribution Constants for B18C6 and 1:1:1 B18C6-Alkali Metal Picrate Complexes at 25 °C

No.	Solvent	$\log K_{\mathrm{D,L}}$[a]	$\log K_{\mathrm{D,MLA}}$		
			Na	K[b]	Rb
1	DCM	2.52	3.36	3.23	3.49
2	CF	2.569	2.92	2.81	3.24
3	1,1-DCE	1.442	—	1.94	—
4	1,2-DCE	2.009	2.97	2.69	3.07
5	CBu	0.369	0.57	0.51	0.66
6	BZ	0.943	1.18	0.95	1.18
7	TE	0.639	0.84	0.93	0.84
8	*m*X	0.301[c]	0.52	0.49[d]	0.45
9	CB	1.155	1.75	1.78	1.97
10	BB	1.130	1.73	1.73	1.96
11	*o*-DCB	1.225	1.94	1.95	2.21
12	DBE	−0.68[e]	−1.12	−1.13[d]	−1.24

a) Ref. 1. b) Recalculated from the data on Ref. 1. c) $K_{\mathrm{D,L}}=2.00\pm0.04$.[f] d) This study. e) $K_{\mathrm{D,L}}=0.21\pm0.02$.[f] f) The average of 15—20 measurements. The uncertainties are the standard deviations.

Table 4. Fundamental Equilibrium Constants, Molar Volumes, and Solubility Parameters at 25 °C

L=B18C6		M		
		Na	K	Rb
$\log K_{\mathrm{MLA}}$		1.54±0.16	3.30±0.20	3.11±0.24
$\log K_{\mathrm{MA}}$[a]		1.38	1.64	1.94
$\log K_{\mathrm{ML}}$[b]		1.38	1.744	1.15
	L	MLA		
V	252±28	366±34	354±32	393±35
δ	11.4±0.1	11.4±0.1	11.4±0.1	11.4±0.1

a) Ref. 5. b) Ref. 6.

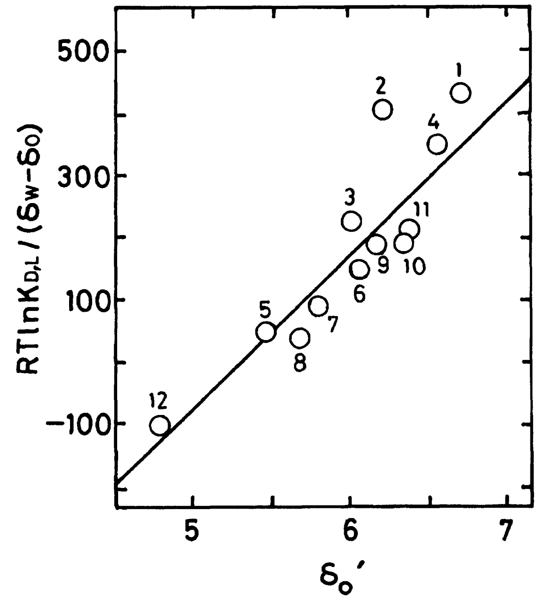

Fig. 4. $RT\ln K_{\mathrm{D,L}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ vs. $\delta_{\mathrm{o}}{}'$ plots for B18C6. The numbers correspond to those in Table 1.

tive M(B18C6)A complexes, except for CF (the correlation coefficients $r=0.966$ for Na, 0.965 for K, and 0.970 for Rb). Positive deviations are also observed for CF. This reflects hydrogen bonds between the B18C6 complexes and CF. For CF, the deviation of the experimental $\log K_{\mathrm{D}}$ value of B18C6 from the calculated one based on regular solution theory is larger than that of each M(B18C6)A complex (Figs. 4, 5, 6, and 7). It follows from this that hydrogen bonds of CF to ether oxygen atoms of B18C6 when B18C6 is complexed are decreased as a result of ionic $\mathrm{M^+}$–O bonding. Except for CF, V and δ for each M(B18C6)A complex were determined from the slope and the intercept, respectively. They are listed in Table 4. The δ_{MLA} values are identical with the δ_{B18C6} value, indicating the validity of Eq. 17. All of the $RT\ln K_{\mathrm{D,MLA}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ vs. $\delta_{\mathrm{o}}{}'$ plots give a better correlation than the $RT\ln K_{\mathrm{D,L}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ vs. $\delta_{\mathrm{o}}{}'$ plots. This is attributed to the stronger hydration and/or the stronger interaction of B18C6 with some organic solvents, compared with the M(B18C6)A complexes; moreover, the worse correlation is probably caused by the variable V_{B18C6} value with the diluent because of the higher flexibility of B18C6.

In general, except for the cases of K and Rb for 1,2-DCE, the $\log K_{\mathrm{D,MLA}}$ values for the same solvent are approximately equal, regardless of the nature of the central alkali metal ion, resulting in the fact that no large difference is found among the V_{MLA} values, and that the δ_{MLA} values are the same (Table 4). For CF, the $\log K_{\mathrm{D,MLA}}$ values of Na and K are much the same. This indicates that the central alkali metal ions are effectively screened from solvents by the B18C6 and pic-

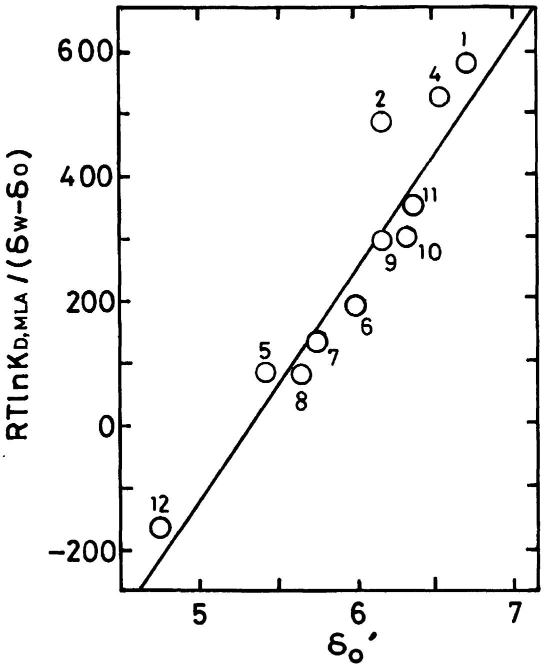

Fig. 5. $RT\ln K_{\mathrm{D,MLA}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ vs. δ_{o}' plots for a B18C6–sodium picrate complex. The numbers correspond to those in Table 1.

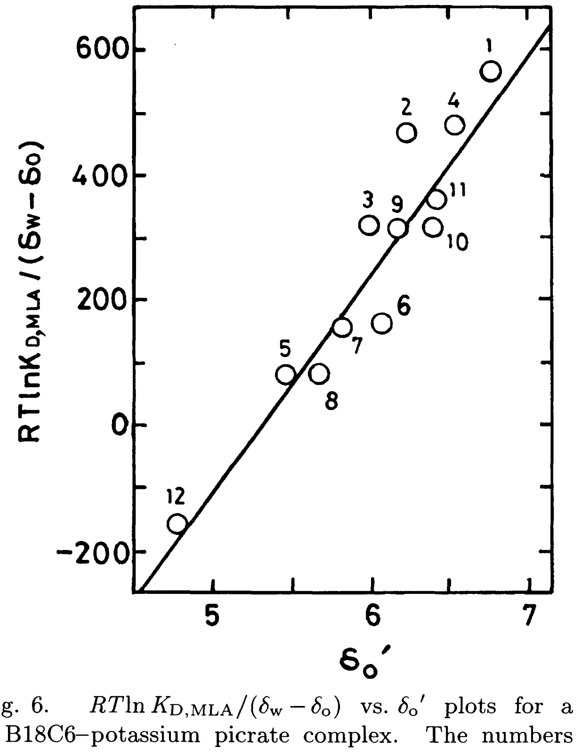

Fig. 6. $RT\ln K_{\mathrm{D,MLA}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ vs. δ_{o}' plots for a B18C6–potassium picrate complex. The numbers correspond to those in Table 1.

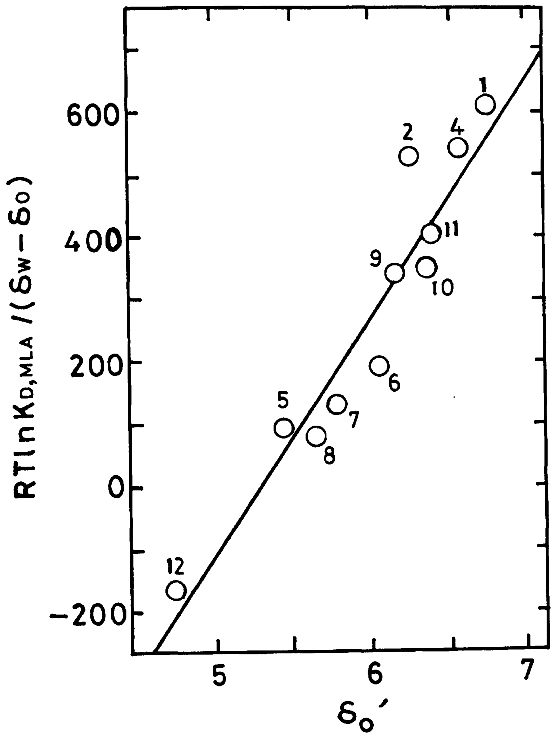

Fig. 7. $RT\ln K_{\mathrm{D,MLA}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ vs. δ_{o}' plots for a B18C6–rubidium picrate complex. The numbers correspond to those in Table 1.

rate ions. Table 3 shows that, for the same solvent, the $|\log K_{\mathrm{D,MLA}}|$ values are larger than the $|\log K_{\mathrm{D,L}}|$ value. This is completely due to the greater V_{MLA} values than the V_{L} value, because the δ_{MLA} and δ_{L} values are equal. The B18C6 and M(B18C6)A complexes are hydrophilic for the DBE system, but the reverse is true for the others. The negative $\log K_{\mathrm{D,L}}$ and $\log K_{\mathrm{D,MLA}}$ values of DBE are attributable to the smaller δ_{o} value and the larger V_{o} value compared with the other solvents (Table 2).

The plots of $\log K_{\mathrm{D,MLA}}$ against E_{T} for the organic solvents in Fig. 8 show a linear relationship. The largest deviation from the straight line is observed for CF.

The $\log K_{\mathrm{KLA}}$ value is slightly larger than the $\log K_{\mathrm{RbLA}}$ one, but the reverse is true for the $\log K_{\mathrm{MA}}$ values. The stronger hydration of K^+ causes a smaller $\log K_{\mathrm{KA}}$ value compared with Rb^+.[5] For K and Rb, the $\log K_{\mathrm{MLA}}$ value is much greater than the corresponding $\log K_{\mathrm{MA}}$ one. For the nitrobenzene extraction system, K^+ and Rb^+ complexes with B18C6 lose virtually all of the water molecules upon complexation.[7] It can thus be considered that both the B18C6–K^+ and –Rb^+ complexes form metal ion-contact ion-pairs with picrate ions. It has been reported that a 18-crown-6 (18C6) complex with K^+ in water has the D_{3d} conformation.[8] It follows from this that the structure of the B18C6 complexes with K^+ and Rb^+ in water is similar to the D_{3d} conformation. The V_{KLA} value is smaller than the V_{RbLA} one. From the above discussion, it can be concluded that a picrate ion is directly in contact with the central alkali metal ion (K^+, Rb^+) in the direction perpendicular to the plane of the B18C6 ring. The $\log K_{\mathrm{MA}}$ value is smaller for Na than for K and Rb. This is due to the strongest hydration of Na^+.[5] Most of water molecules attached to Na^+ are released upon

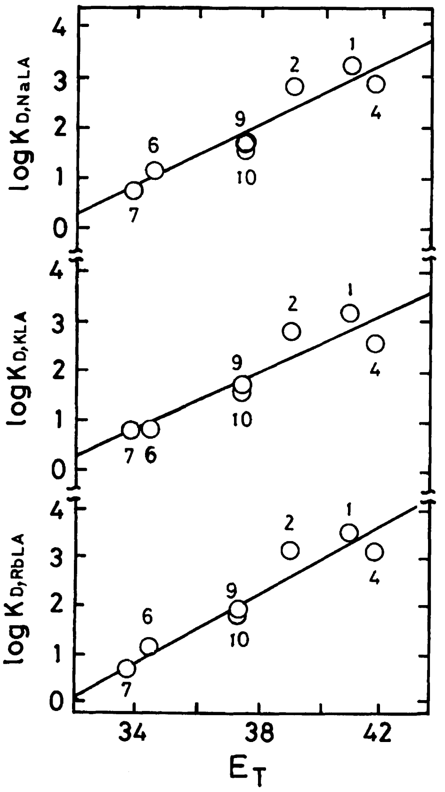

Fig. 8. $\log K_{\mathrm{D,MLA}}$ vs. E_{T} plots for B18C6–alkali metal picrate complexes. The numbers correspond to those in Table 1.

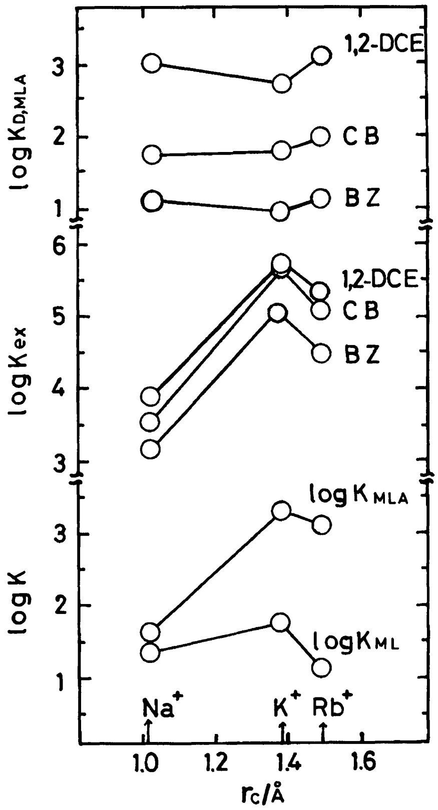

Fig. 9. Plots of $\log K_{\mathrm{MLA}}$, $\log K_{\mathrm{ML}}$, $\log K_{\mathrm{ex}}$, and $\log K_{\mathrm{D,MLA}}$ vs. crystal ionic radii (r_{c}) of alkali metals.

complexation with B18C6 for the nitrobenzene extraction system.[7] The same can be expected to hold for the diluent systems used in this study. A Na^+ complex with 18C6 has the C_1 conformation in water; the Na^+ ion is wrapped with 18C6.[8] The Na^+ complex with B18C6 in water probably prefers a similar conformation. It thus appears that the conformation of the B18C6 complex prevents a picrate ion from approaching the central Na^+ ion. Consequently, the $\log K_{\mathrm{MLA}}$ value is much smaller for Na than for K and Rb; the $\log K_{\mathrm{NaLA}}$ value is slightly larger than the $\log K_{\mathrm{NaA}}$ one. The above discussion may also be supported by the fact that the V_{MLA} value of Na is nearly equal to that of K. If the Na^+–B18C6 complex prefers the D_{3d} conformation and a picrate ion is directly in contact with the Na^+ ion held in the cavity, the V_{NaLA} value is expected to be smaller than the V_{KLA} value.

The $K_{\mathrm{D,MLA}}$ and $K_{\mathrm{D,L}}$ values related to the distribution behavior cancel each other; therefore, in the cases of K and Rb, the K_{ex} value depends largely on the K_{MLA} value; the K_{ex} value of Na is determined mainly by both the K_{ML} and K_{MLA} values (Eq. 7). Plots of $\log K_{\mathrm{D,MLA}}$ and $\log K_{\mathrm{ex}}$ for some representative diluents, $\log K_{\mathrm{MLA}}$, and $\log K_{\mathrm{ML}}$ against crystal ionic radii of alkali metals are shown in Fig. 9. For every diluent system, the extraction-selectivity order of B18C6 for the alkali metal ions is $\mathrm{K}^+ > \mathrm{Rb}^+ > \mathrm{Na}^+$ (Table 1). Table 3 and Fig. 9 show that the $\log K_{\mathrm{D,KLA}}$ value makes no contribution to the highest extraction-selectivity for K^+. The higher extractability of K^+ is more attributable to the greater $\log K_{\mathrm{ML}}$ value than to the slightly larger $\log K_{\mathrm{MLA}}$ value compared with Rb^+, whereas the much higher extractability of K^+ is far more dependent on the much larger $\log K_{\mathrm{MLA}}$ value than on the greater $\log K_{\mathrm{ML}}$ value compared with Na^+. Although the B18C6 complex with Rb^+ is less stable in water than that with Na^+, Rb^+ is more extractable than Na^+. This is largely due to the much larger $\log K_{\mathrm{MLA}}$ value of Rb than that of Na.

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